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Rate Enhancement Resulting from Reagent Vibrational Excitation as Estimated by the BEBO Method

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The bond-energy bond-order (BEBO) method for calculating rate coefficients and activation energies on the basis of molecular properties has been applied to estimating rate coefficients and activation energies for H-transfer reactions involving vibrationally excited reactants. The reactions examined included Br + H_2(v = 0, 1) = H + HBr, Br + HCl(v = 0, 1, 2) = Cl + HBr, and F + HCl(v = 0, 1) = Cl + HF. Good agreement was obtained between the computed BEBO rate coefficients and published rate coefficients. It is

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important to note that the rate enhancement resulting from vibrational excitation could be explained for most of the reactions as being largely caused by the lower bond dissociation energy of the vibrationally excited reagent. Because of the significance of vibrational de-excitation rates in chemical lasers, BEBO computations were made for HF and DF de-excitation by reactions with H, D, F, and other atoms. The highest computed de-excitation rate coefficients were those involving reactions with F-atoms. Reagent vibrational excitation to v = 10 was examined. Computations were also made to estimate rate coefficients for several possible deuterium isotope separation methods based on the use of vibrationally excited reactants.

PREFACE

We are grateful to K. Foster for carrying out all the computer calculations discussed in this report.

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I. INTRODUCTION

In a recent report,[1] it was shown that the bond-energy bond-order (BEBO) method[2,3,4] provided good agreement between measured and computed rate coefficients for the reaction of F with H_2 or D_2. Additionally, population inversions could be predicted with this method because the computed rate coefficients for the production of vibrationally excited HF and DF were larger than for ground-state HF and DF.[1] Consequently, we investigated the applicability of the BEBO method for estimating the effect of reactant vibrational excitation on enhancing the kinetics of such reactions as

$$A + HB(v = 0,1,2, \ldots) = B + AH$$

Reactions of this type have been of considerable importance in connection with de-excitation in high-power chemical lasers,[5,6] isotope separation by selective laser excitation,[7] and research in excited-state kinetics.[8,9,10]

The BEBO method was developed[2] to provide convenient and rapid computations for estimating rate coefficients and activation energies of hydrogen-transfer reactions. The method utilizes known molecular parameters such as bond-dissociation energies, bond lengths, and vibration frequencies; it is based on the principles of small-vibration dynamics in molecules and on transition-state theory; and it has provided satisfactory agreement with many measured rate coefficients.[2,3,4] No adjustable parameters are required with this method, and it is much briefer computationally than *ab initio* quantum mechanical methods[11] or the London-Eyring-Polanyi-Sato (LEPS) transition-state procedure, which requires calculations for a relatively large potential energy surface.[12]

II. COMPUTATION METHOD FOR REACTIONS INVOLVING EXCITED STATES

The BEBO method is based on the concept that energy released as the product AH is formed can supply part or all of the energy needed during the breaking of the reactant HB bond. If the energy available as the bond order of product AH increases from zero to one is less than the energy needed as the bond order of reactant HB decreases from one to zero, the difference is computed as the potential energy of activation. This difference is calculated by the computer program on the basis of the following BEBO method trial assumptions:[2]

1. The Pauling rule for the relationship between bond length and bond order applies in the transition state.

2. The Lennard-Jones 6-12 energy and distance parameters for the noble gases represent the zero-order bond energies and internuclear distances for elements in the corresponding row of the periodic table.

3. The triplet repulsion that results from uncoupled spins is represented by a Sato anti-Morse function similar to that for the triplet $^3\Sigma_u^+$ state of H_2.

4. The logarithm of bond energy is proportional to the logarithm of bond order.

The Sato triplet repulsion is a function of the bond dissociation energy of the compound AB. For a typical excited-state reaction such as H + HF(v = 1) = F + H_2, note that the bond-dissociation energy of the vibrationally excited reagent is considerably less than that for the ground-state reagent. Consequently, a bond-dissociation energy for the triplet repulsion that is proportionately lower than that for the ground state is used by the BEBO computations for excited states. For example, in the computation for this reaction of an H atom with HF (v = 1) to produce ground-state H_2, the dissociation energy used for triplet repulsion is that for HF(v = 1), namely, 123.8 kcal/mole, as given in Table 1. In this example, the value of 103.3 kcal/mole would be used as the dissociation energy of H_2. Bond dissociation energies of excited states were obtained from Reference 6. Molecular parameters used for these BEBO calculations are listed in Table 1.

Table 1. Molecular Parameters

Reagent	Bond Dissociation Energy,[a] kcal/mol	Bond Dissociation Energy for First Vibrational Level,[b] kcal/mol	Interatomic Distance,[c] 10^{-8} cm	Vibrational Wave Number,[c] cm^{-1}
OH	101.3	91.1	0.971	3735
HBr	86.6	79.3	1.41	2650
HCl	102.3	94.1	1.28	2990
HF	135.1	123.8	0.917	4138
DF	135.7	127.4	0.917	2998
H_2	103.3	91.4	0.742	4405
D_2	105.0	96.5	0.742	3119

[a]Ref. 13.

[b]Ref. 6.

[c]Ref. 14.

The trial assumptions have provided satisfactory agreement between computed and experimental rate coefficients and activation energies for several reactions.[1-4] Nevertheless, such assumptions are primarily empirical, and calculations made on the basis of these assumptions must be considered to be only estimates of the rate coefficients and activation energies for the reactions under consideration.

III. RESULTS AND DISCUSSION

A. $Br + H_2$

The rate-enhancing effect of vibrational excitation of H_2 to the first vibrational level was the subject of trajectory calculations by Sims, Dosser, and Wilson[9] for the reaction

$$Br + H_2(v = 0, 1) = H + HBr \tag{1}$$

at 600 and 800 K. The results of these calculations were 3.7×10^4 at 600 K and 3.1×10^3 at 800 K for k_1/k_0, the ratio of the rate coefficient for $v = 1$ to the rate coefficient for $v = 0$. The corresponding values of k_1/k_0 obtained by our BEBO computation procedure are 2.9×10^4 at 600 K and 2.1×10^3 at 800 K. According to the BEBO computations, furthermore, it is predicted that, at lower temperatures, the rate-enhancing effect of H_2 excitation would be greater. Thus, the computed BEBO values of k_1/k_0 are 9×10^8, 5×10^7, and 2×10^5 at 300, 400, and 500 K, respectively. This trend results because the computed BEBO activation energy decreases to 8.3 kcal/mole for $v = 1$, compared to 20.7 kcal/mole for $v = 0$.

B. $Br + HCl$

The kinetics effect of vibrational excitation of HCl by a pulsed chemical laser was measured by Arnoldi and Wolfrum[15] for the reaction of HCl with Br

$$Br + HCl(v = 0, 1, 2) = Cl + HBr \tag{2}$$

They observed a vibrational enhancement[10,15] of 2×10^6 for k_1/k_0. The computed BEBO k_1/k_0 is 1.53×10^6. The measured[1,3] enhancement for the second vibrational level of HCl was 1×10^{11} for k_2/k_0; the BEBO result is 5×10^{11}.

The computed BEBO activation energy for $HCl(v = 2)$ in this reaction was 0.5 kcal/mole, in contrast to BEBO activation energies of 8.6 kcal/mole and 16.9 kcal/mole for $HCl(v = 1)$ and $HCl(v = 0)$, respectively. It has previously been indicated[3] that the BEBO method cannot be expected to provide reliable computations of rate coefficients for certain reactions in which the bending-force constant of the transition state is so low that the bending amplitude of the transition state becomes unrealistically high at temperatures above 273 K. The BEBO calculations for $HCl(v = 3, 4, 5)$ in reaction (2) revealed that this bending-force constant did become too low to permit reliable calculations of the corresponding rate coefficients. This effect was encountered in calculations for very high vibrational excitation in many of the reactions, which will be discussed in this report. When the reagent vibrational excitation is sufficiently high, the height of the potential energy barrier approaches zero; consequently, the transition state calculations become unreliable.

C. F + HCl

As part of an extensive series of pioneering studies in Polanyi's laboratory, measurements[16,17] were made to determine the effect of HCl vibrational excitation on the reaction

$$F + HCl(v = 0, 1) = Cl + HF \tag{3}$$

The measured k_1/k_0 was in the range of 3 to 9; the computed BEBO value of k_1/k_0 is 3.5, in sufficient agreement. The BEBO activation energies are 1.4 and 1.2 kcal/mole for v = 0 or 1. Reactions (1) and (2) are strongly endothermic for v = 0, whereas reaction (3) is exothermic. Nevertheless, the computed BEBO results are generally in good agreement with the measured or trajectory values for rate enhancement owing to vibrational excitation. It has previously[1,2] been explained that the BEBO method is based on a model

$$BH + A = B \underset{n}{\cdots} H \underset{m}{\cdots} A = B + HA \tag{4}$$

where, in the transition state B ... H ... A, the bond-order m of the new bond is increasing from zero to one, while the bond n of the breaking bond B...H is simultaneously decreasing from one to zero. With the BEBO model, the energy available from the formation of the H...A bond can be used to supply part or all of the energy required for dissociating the B...H bond. A potential-energy barrier develops for most H-transfer reactions because the energy available during the formation of H...A does not supply all the energy needed during the dissociation process for the reagent B...H. However, this BEBO model suggests that, if the reagent is vibrationally excited and consequently requires less energy for its dissociation, the resultant activation energy barrier is expected to be lower than for the case when v = 0 for reagent BH. The BEBO computations were generally in agreement with this expectation. The explanation of many cases of enhanced rates resulting from reagent vibrational excitation would, therefore, simply be based on the lower bond dissociation energy of the excited reagent plus the coordinated availability of energy from the formation of the new bond H...A. In the BEBO model, this coordination arises from maintaining the sum of the bond orders n and m equal to 1.00, inasmuch as one bonding orbital on H is transferring from B to A during the reaction.

D. $\underline{H + H_2}$

Heidner and Kasper[18] measured the predominantly reactive increase in rate coefficient resulting from excitation of H_2 for

$$H + H_2(v = 0,\ 1) = H + H_2 \qquad (5)$$

They obtained a value of about 1500 for k_1/k_0 at 300 K. The computed BEBO value for k_1/k_0 is 6000, and the activation energy for v = 1 is 3.8 kcal/mole compared to 9.0 kcal/mole for v = 0.

E. $O + H_2$

For the reaction

$$O + H_2(v = 0, 1) = H + OH \qquad (6)$$

Light[19] measured k_1/k_0 to be 2600. The computed BEBO k_1/k_0 is 5400, and the computed activation energies are 5.7 and 10.8 kcal/mole for v = 1 and 0, respectively.

F. $O + HCl$

MacDonald and Moore[20] measured the rate constant for the reaction

$$O + HCl(v = 1) = Cl + OH \qquad (7)$$

and found it to be 5×10^{11} cm^3/mole-sec. The computed BEBO rate constant is 3×10^{11} cm^3/mole-sec. The computed BEBO value of k_1/k_0 is 45, with the energies of activation equal to 2.6 and 1.8 kcal/mole for v = 0 and 1, respectively.

G. $D + HCl$

Kneba[21] used time-resolved mass spectroscopy and atomic resonance absorption to determine the rate coefficient at 298 K for the reaction of HCl(v = 1) with D to produce DH and Cl. The measured rate coefficient was 2.6×10^{11} cm^3/mole-sec, whereas the computed BEBO rate coefficient at 300 K is 2×10^{11} cm^3/mole-sec. The BEBO activation energy is 3.0 kcal/mole.

H. $I + HCl$

Kaplan, Levine, and Manz[22] applied their information theory (surprisal) method to computing rate coefficients at 300 K for the reaction of HCl(v) with and iodine atom to form HI and Cl, making use of the experimental rate coefficients for the reverse reactions. The computed BEBO rate coefficients are in fair agreement with their results. For values of v = 0, 1, 2, 3, and 4, the ratios of the BEBO rate coefficients at 300 K to their surprisal rate coefficients are, respectively, 2.9, 3.2, 1.3, 1.1, and 2.2. Figure 1 reveals the

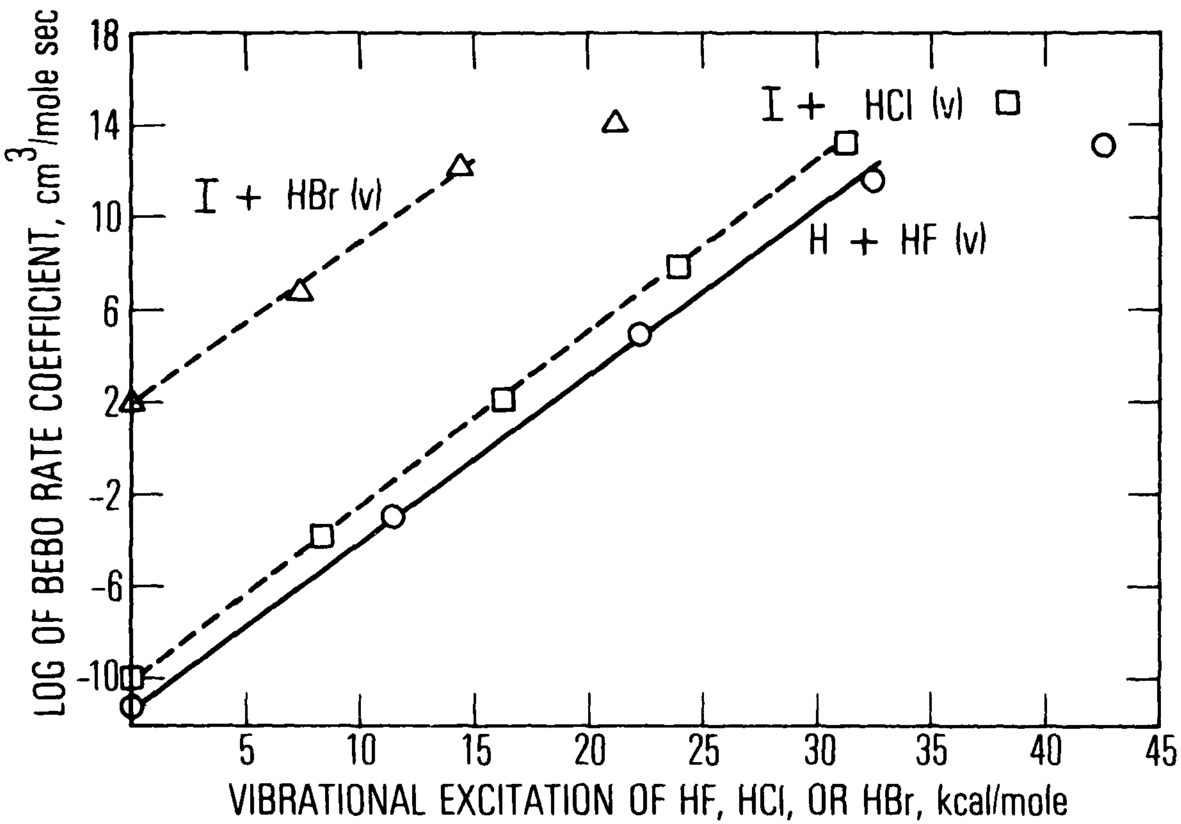

Figure 1. Dependence of log of BEBO Rate Coefficient on Reagent Excitation

dependence of the BEBO rate coefficients on the vibrational excitation of HCl. There is an almost linear dependence of log k_v on the vibrational excitation of HCl(v) up to a v of 4. This approximate linearity occurs because the computed BEBO decrease in the height of the potential energy of activation barrier for v = 1, 2, 3, or 4 corresponds very closely (average deviation only 0.11 kcal/mole) with the increase in HCl vibrational excitation energy (Cohen and Bott[6]) for v = 1, 2, 3, and 4. The reaction becomes exoergic, however, for v = 5, and the BEBO decrease in barrier height is typically much less than the increase in reagent excitation for exoergic reactions for HCl(v = 0, 1, 2, 3, 4).

The importance of minimizing reactive de-excitation of vibrationally excited HF or DF is well recognized[6] by workers concerned with increasing the power from HF or DF laser. The BEBO method can provide a convenient and economical way to estimate rate coefficients for such reactions. When measured de-excitation rate coefficients do not exist for the de-excitations of interest, the BEBO results can be utilized in the several available computer codes for modeling the behavior of chemical lasers. The results of a typical BEBO de-excitation computation are given in Table 2 for the chemical laser reaction in which excited HF is lost by reaction with H

$$H + HF(v = 0 - 10) = F + H_2(v' = 0,1) \tag{8}$$

The BEBO method uses so little computer time that it is economical to make calculations for values of v as high as 10 and also to include reactions in which the product is excited to v′ = 1. Furthermore, it was a standard procedure in this series of computations to obtain the results for temperatures of 100, 400, 500, 600, 800, 1000, 1200, and 1400 K, as well as 300 K. Values were also computed for the activation energy (E_a) and the potential energy of activation (V^*). In Table 2, ΔB is the bond dissociation energy of the reagent minus the bond dissociation energy of the product.

Table 2. BEBO Estimates of Rate Coefficients for $H + HF(v = 0 - 10) = F + H_2(v' = 0, 1)$

v	Rate Coefficients at 300 K, cm^3/mol-sec				
	$v' = 0$	$v' = 1$	E_a, kcal/mole	V^*, kcal/mole	ΔB, kcal/mole
0	0.41×10^{-11}	0.38×10^{-19}	34.6	33.2	+31.8
1	0.91×10^{-3}	0.11×10^{-10}	23.0	21.9	+20.5
2	0.11×10^{6}	0.13×10^{-2}	11.7	11.8	+ 9.6
3	0.40×10^{12}	0.48×10^{5}	2.7	4.4	- 0.7
4	0.11×10^{14}	0.21×10^{13}	1.3	1.1	-10.6
5	0.78×10^{14}	0.30×10^{14}	1.2	0.2	-20.0
6	0.73×10^{15}[a]	0.33×10^{15}[a]			
7	0.34×10^{16}[a]	0.34×10^{16}[a]			
8	0.61×10^{16}[a]	0.61×10^{16}[a]			
9	0.12×10^{17}[a]	0.11×10^{17}[a]			
10	0.26×10^{17}[a]	0.25×10^{17}[a]			

[a]At these values of v, the computed values of the bending-force constant in the transition state were so low that small vibration dynamics (and BEBO) do not apply.[2,3]

The results given in Table 2 are typical of reactions that are strongly endothermic when the reagent is in the ground state. For v = 0, the corresponding rate coefficient (k_0) is so small that rates would be extremely slow. For v = 1, the rate coefficient (k_1) increases by a factor of more than 2×10^8, but the rate of de-excitation of HF(v = 1) by reaction with H would be small on the time scale of a typical chemical laser. However, for HF excited to v = 4 or 5, the rate coefficients for de-excitation by reaction with H are quite large and are significant for affecting the behavior of HF lasers. Depending on the characteristics of the chemical laser, the de-excitation of HF(v = 3) by H might be appreciable. In Table 2, it is evident that ΔB, E_a, and V^* decrease when v increases. As the reaction becomes more exothermic (for example, at v = 4), the changes in rate coefficient and activation energy become smaller. In Fig. 1, the dependence of log b_v on HF excitation is fairly linear for v = 1 or 2. However, when ΔB becomes negative at higher values of v, the increases in log k_v become comparatively smaller because the decreases in BEBO E_a and V^* are less than the corresponding decreases in ΔB. For v = 4 or 5 (Table 2), the rate coefficients for the formation of vibrationally excited product $H_2(v = 1)$ may be significant also. In Table 2, the superscript a is used to denote those cases (at relatively high values of v and exothermicity) for which the computed bending force constants in the transition state are so low that the amplitudes of vibration in the transition state are unrealistically[2,3] large and the potential energy of activation is virtually nil. In such cases BEBO rate coefficients should not be used because BEBO relies on transition state theory; instead, it is believed[2] preferable to use collision theory to calculate rate coefficients.

Table 3 is a summary of the BEBO results for computations similar to those made for Table 2. Any oxygen atoms present in the chemical laser gases would have HF de-excitation rate coefficients somewhat larger than those for hydrogen atoms at v higher than 2. An atom, such as Br, which reacts more endothermically with HF(v), would generate lower de-excitation rate coefficients. When v is 5 or higher, however, it appears that almost any atom or radical present in the laser gas could react rapidly with HF(v) to de-excite it. Bernstein has observed[10] that reactions that are

Table 3. Rate Coefficients[a] for De-excitation of HF(v) and HCl(v)

v	$O + HF(v) \rightarrow F + OH$	$Br + HF(v) \rightarrow F + HBr$	$H + HCl(v) \rightarrow Cl + H_2$
0	1.1×10^{-12}	5.2×10^{-23}	8.5×10^{9}
1	2.4×10^{-4}	1.4×10^{-14}	2.3×10^{11}
2	2.7×10^{4}	1.9×10^{-6}	2.2×10^{12}
3	6.4×10^{12}	9.2×10	1.3×10^{13}
4	2.2×10^{13}	2.2×10^{9}	4.4×10^{13}
5	1.3×10^{14}	5.0×10^{14b}	1.5×10^{14}
6	1.7×10^{15b}	8.0×10^{14b}	7.1×10^{14b}

[a]Rate coefficients at 300 K, cm^3/mole-sec.
[b]Bending force constant of transition state is too low.

strongly endothermic for ground-state HF have a vibrational threshold effect. The BEBO results for HF are consistent with this observation because the rate coefficients for the lower values of v in Tables 2 and 3 are so small that the experimentally measured rates could be extremely low compared to the rates for $v = 4, 5,$ or 6. For the more thermoneutral reaction of H with HCl, however, it is evident in Table 3 that the rate coefficients do not increase so rapidly as a function of v.

In Table 4, results are summarized for BEBO computations involving DF(v). The removal rates for HF(v) are important, of course, for DF lasers.[6] A comparison of the rate coefficients in Table 2 with those for H + DF(v) (Table 4) at equal values of v indicates that the removal rate coefficients for H + DF are generally lower than those for H + HF(v). This difference is probably largely the result of the lower exothermicity for the H + DF(v) reactions because of the closer spacing of the DF vibrational levels. The larger computed BEBO rate coefficients for the D + DF(v) reactions can be attributed to the lower vibration frequency of D_2 compared to that for DH. The calculated de-excitation rate coefficients for D + DF(v) at $v = 3, 4, 5,$ or 6 are considerably smaller than those for H + HF(v). This factor could contribute to higher laser power for the DF laser than for the HF chemical laser at higher vibrational transitions.

In the last two columns of Table 4 are the rate coefficients for DF(v) de-excitation by means of exchange reactions involving D atom transfer. Note that the rate coefficients for de-excitation of DF(v) by F are considerably higher than those for DF(v) de-excitation by D. This fact might indicate that obtaining higher power from DF chemical lasers would be facilitated by minimizing the quantity of F-atoms present in the laser gases after the $F + D_2 = DF(v) + F$ results in rapid de-excitation by the nearby F atoms exchanging with the DF(v). The high endothermicity of the D + DF reaction is the probable reason that these rate coefficients are smaller than those for the F + DF reaction. The BEBO results apply only to reactive and not to nonreactive de-excitations. The values in the last column of Table 4 differ from those of the next-to-last column because the DF of the last column has been de-excited to the $v - 1$ level rather than to the $v = 0$ level. In the BEBO method, it is

Table 4. De-excitation Rate Coefficients[a] for DF(v)

v	$D + DF(v) \rightleftarrows F + D_2$	$H + DF(v) \rightleftarrows F + HD$	$F + DF(v) \rightleftarrows FD(v = 0) + F$	$F + DF(v) \rightleftarrows FD(v - 1) + F$
0	0.38×10^{-10}	0.39×10^{-11}	0.13×10^{12}	--
1	0.46×10^{-4}	0.58×10^{-5}	0.44×10^{13}	0.44×10^{13}
2	0.34×10^{2}	0.42×10	0.19×10^{14}	0.10×10^{14}
3	0.12×10^{8}	0.16×10^{7}	0.17×10^{15}	0.19×10^{14}
4	0.17×10^{12}	0.36×10^{11}	0.16×10^{16b}	0.77×10^{14}
5	0.56×10^{13}	0.27×10^{13}	0.22×10^{16b}	0.22×10^{15b}
6	0.29×10^{14}	0.18×10^{14}	0.26×10^{16b}	0.30×10^{15b}
7	0.13×10^{15}	0.82×10^{14}		
8	0.10×10^{16b}	0.50×10^{15b}		
9	0.42×10^{16b}	0.27×10^{16b}		

[a]Rate coefficients at 300 K, cm^3/mole-sec.
[b]Bending-force constant of transition state is too low.

to be expected that the rate coefficients for DF(v - 1) production would be smaller than those for ground-state DF production because the bond energy is smaller for DF(v - 1) than for ground state DF if v is at least 2. However, consideration of the transition state F...D...F for this reaction indicates that extra energy may be required to dissociate FDF because of the formation of a hydrogen bond such as that occurring in hydrogen fluoride vapor.[23] This extra bond energy can range from 2 to 10 kcal/mole. BEBO calculations were made in which this possible additional stability for FDF was considered; the calculated rate coefficients were found to be lowered by a factor of one hundred for 10 kcal/mole stabilization. Such extra bond energy for FDF could possibly be the reason that the BEBO rate coefficients are higher (Table 4) for the loss of several vibrational quanta than for the loss of one quantum, whereas calculations by Wilkins[24] indicate higher rate coefficients when only one vibrational quantum is lost. BEBO computations were also made for de-excitation of HF(v) by exchange reactions. For the reaction F + HF(v = 1) = F + HF, the calculated rate coefficient was 0.13×10^{14} at 300 K. This value is much higher than for HF(v = 1) de-excitation by H (Table 2). For v > 1, the bending-force constants were too low; this indicates much faster de-excitation of HF(v) by F atom exchange than by reaction with H atoms.

IV. BEBO CALCULATIONS FOR DEUTERIUM ISOTOPE SEPARATION REACTIONS INVOLVING VIBRATIONALLY EXCITED REAGENTS

Because of the desirability of developing more economical methods of producing D_2O for use in heavy-water moderated nuclear power reactors, there has been speculation on the bimolecular reaction rate enhancement obtainable by selective excitation of deuterium compounds.[25] In Table 4, note that the BEBO method estimate for the rate coefficient of the reaction of DF(v = 5) with H to produce DH is 0.27×10^{13} cm^3/mole-sec, whereas the rate coefficient of the same reaction for ground state DF or HF is less than 0.5×10^{-11} cm^3/mole-sec. Because of the endothermicity of this reaction, however, it would be necessary to expend enough energy to excite DF to its fifth vibrational level in order to achieve this desirable enhancement of the rate coefficient. BEBO method results for less endothermic reactions of deuterium compounds are summarized in Table 5. These reactions do not require as much excitation of the deuterium compounds as do more endothermic reactions, in order to achieve rates that could yield adequate productivity. As an example (Table 5), DF(v = 2) reacting with OH has a rate coefficient of 0.22×10^{12} cm^3/mole-sec, compared to 4.2 cm^3/mole-sec for the H + DF(v = 2) reaction. The BEBO rate coefficients for OH + DF with v equal to 3 or 4 were 0.30×10^{13} or 0.33×10^{14} cm^3/mole-sec, respectively. These k_r's are also much higher than the corresponding k_r's for H + DF in Table 4. The decrease in ΔB (the difference in bond dissociation energies for product and reactant) for the OH + DF reaction is 16.4 kcal/mole when v changes from 0 to 2 (Table 5). The corresponding decrease in activation energy is 16.3 kcal/mole as computed by the BEBO method. This computation reveals that the vibrational excitation of DF can be used efficiently to lower the activation energy barrier for DF reactions. However, at higher values of v the decrease in reaction endothermicity may reduce the efficiency of vibrational excitation for lowering the activation energy. For example, in the OH + DF reaction, ΔB decreases by 15.3 kcal/mole when v rises from 2 to 4, but the computed E_a drops by only 1.7 kcal/mole.

Table 5. BEBO Rate Coefficients[a] for Reactions of Vibrationally Excited Deuterium Compounds

	$OH + DF(v) = F + DOH$			$O + DCl(v) = Cl + OD$			$H + DCl(v) = Cl + DH$		
v	k_r	E_a	ΔB	k_r	E_a	ΔB	k_r	E_a	ΔB
0	0.27	19.3[b]	17.7[b]	0.20×10^{7}	9.2	1.0	0.46×10^{10}	5.1	-1.8
1	0.44×10^{6}	10.6	9.4	0.59×10^{11}	3.1	-5.0	0.87×10^{11}	3.6	-7.8
2	0.22×10^{12}	3.0	3.0	0.69×10^{15}[c]	0.0	-10.8	0.65×10^{12}	2.7	-13.6

	$Cl + DCF_3(v) = CF_3 + DCl$			$O + DCF_3(v) = CF_3 + OD$			$Br + DCCl_3(v) = Cl_3 + DBr$		
v	k_r	E_a	ΔB	k_r	E_a	ΔB	k_r	E_a	ΔB
0	0.46×10^{10}	5.0	2.7	0.10×10^{-1}	20.4	3.7	0.56×10^{11}	3.9	2.4
1	0.97×10^{13}	0.5	-1.9	0.15×10	17.6	-0.9	0.58×10^{14}	0.6	-1.8
2	0.57×10^{15}[c]	0.0	-6.3	0.91×10^{2}	15.1	-5.3	0.75×10^{15}[c]	0.1	-5.8

[a] Rate coefficients at 300 K, cm^3/mole-sec.
[b] Units are kcal/mole for E_a (activation energy) and ΔB.
[c] Bending-force constant of transition state is too low.

Because the bond dissociation energy of DCl is less than that for DF, higher rate coefficients (and greater rates of formation of deuterium compound products) could be obtained at equal values of v although less energy would be needed to excite DCl than DF. The BEBO results in Table 5 for the O + DCl and H + DCl reactions support this possibility. Thus, DF must be excited to v = 4 to obtain (Table 4) a BEBO k_r of 0.36×10^{11} for the H + DF reaction, but a BEBO k_r of 0.87×10^{11} is obtained at v = 1 for the H + DCl reaction (Table 5). Vibrational excitation of DCl to v = 1 appears to be quite efficient for lowering the activation energy barrier of the O + DCl reaction because the BEBO E_a is decreased by 6.1 kcal/mole (Table 5) as a result of DCl(v = 0) being excited by 6.0 kcal/mole to v = 1. It is possible that a DCl discharge lamp could be a satisfactory source of radiation for selectively exciting DCl (in a natural mixture of DCl and HCl) to v = 1 with rotational quantum numbers from 0 to 10. The BEBO k_r's indicate that this excitation would provide rate coefficients for the D + DCl reaction that are 10^4 to 10^6 larger than the k_r's for reaction with ground-state DCl or HCl.

Inasmuch as the H + DCl reaction is exothermic, vibrational excitation does not cause as large an increase in the BEBO k_r's as it does for the O + DCl reaction. Vibrational excitation of the D-C bond in DCF_3 or $DCCl_3$ can also be effective for enhancing rate constants, as can be seen in the BEBO results of Table 5. For Cl + DCF_3, the computed activation energy barrier was lowered by 4.5 kcal/mole when the D-C bond was excited by 4.6 kcal/mole to v = 1. The BEBO k_r's for O + DCF_3 indicate that this reaction is too slow for satisfactory productivity of OD even when v = 2 for the D-C bond. On the other hand, the BEBO k_r for the Br + $DCCl_3$ reaction is rather large even when v = 1 for the D-C bond. Also, the computed E_a for this reaction decreases by 3.3 kcal/mole when the D-C bond is excited by 4.2 kcal/mole to v = 1.

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